(19)日本国特許庁（ＪＰ）　(12)公開特許公報（A）　(11)特許出願公開番号

特開平11－12735

(43)公開日　平成11年(1999)１月19日

(51)Int.Cl.[6]	識別記号	FI
C２３C　16/26		C２３C　16/26
16/50		16/50

審査請求　未請求　請求項の数４　ＯＬ　（全７頁）

(21)出願番号　特願平9－168682

(22)出願日　平成９年(1997)６月25日

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(54)【発明の名称】　ダイヤモンド状炭素薄膜の製造方法

(57)【要約】
【課題】　大気圧近傍の圧力の下で、ガス雰囲気を問わず、均一な放電プラズマを発生させて、ダイヤモンド状炭素薄膜を基材表面に高速、且つ、低温で製造する方法を提供する。
【解決手段】　大気圧近傍の圧力下で、対向電極の少なくとも一方の対向面に固体誘電体を設置し、炭素並びに酸素及び／又は水素を含有するガス雰囲気下で、当該対向電極間にパルス化された電界を印加することにより放電プラズマを発生させることを特徴とする。

PATENT ABSTRACTS OF JAPAN

(11)Publication number : 11-012735

(43)Date of publication of application : 19.01.1999

(51)Int.Cl. C23C 16/26
C23C 16/50

(21)Application number : 09-168682

(22)Date of filing : 25.06.1997

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(54) PRODUCTION OF DIAMOND-LIKE THIN CARBON FILM

(57)Abstract:

PROBLEM TO BE SOLVED: To rapidly form a thin carbon film with stability at a low temp. by producing plasma by setting a solid dielectric on an opposed plane of at least either of counter electrodes and applying a pulsed electric field between the electrodes under an atmosphere containing carbon and oxygen and/or hydrogen under a pressure in the vicinity of atmospheric pressure.

SOLUTION: Under a pressure of 100 to 800 Torr in the vicinity of atmospheric pressure, a solid dielectric of plastic, glass, etc., is set on one counter electrode plane, and, a pulsed electric field is applied between the counter electrode planes in a gaseous atmosphere containing carbon, oxygen, hydrogen, etc., to carry out electric discharge and produce plasma. In this case, the discharge current density between the counter electrodes is regulated to (0.2 to 300) mA/cm2, and (1 to 100) kv/cm electric field intensity is applied. Further, frequency and pulse duration at this time are regulated to 1 to 100 kHz and 1 to 1000 μs, respectively, by which the thin film can be easily formed on a base-material plane of the surface of the solid dielectric.

LEGAL STATUS

[Date of request for examination] 20.01.2004

[Date of sending the examiner's decision of rejection] 25.01.2006

[Kind of final disposal of application other than the examiner's decision of rejection or

* NOTICES *

1.This document has been translated by computer. So the translation may not reflect the original precisely.
2.**** shows the word which can not be translated.
3.In the drawings, any words are not translated.

DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[Field of the Invention] This invention relates to the approach of manufacturing a diamond-like carbon thin film on the surface of a base material under the pressure near the atmospheric pressure using the discharge plasma.
[0002]
[Description of the Prior Art] The diamond-like carbon thin film has the outstanding physical properties, such as a degree of hardness, a high refractive index, and electric conductivity, and is being used for an application broad as covering material, such as an object for an ornament, an object for tools, and an object for electron devices.
[0003] The approach which the heat CVD method, the plasma-CVD method, the ion beam method, the ion plating method, etc. are learned, for example, forms a diamond-like carbon thin film in JP,58-91100,A with a heat CVD method as the manufacture approach of a diamond-like carbon thin film conventionally using carbon content gas and hydrogen gas is indicated, and the approach of forming membranes by the plasma-CVD method using carbon content gas and inert gas is indicated by JP,64-31974,A.
[0004] However, in order to form membranes in the condition that a degree of vacuum is low, before the generated carbon content active species arrived at the base material front face, these active species collided, the active species of another kind was generated, a pure diamond-like carbon thin film was not formed, but since base material temperature was an elevated temperature 800 degrees C or more, the above-mentioned heat CVD method and the plasma-CVD method had further the fault that membranes could be formed only to a specific base material. Moreover, to the top which needs a vacuum facility, a plasma consistency does not become large but the thin film composition under low voltage conditions has a slow membrane formation rate. Since it is industrially disadvantageous in cost, these do not fit only to expensive processing articles, such as electronic parts and an optic.
[0005] For this reason, the method of processing under the ambient atmosphere which the method of generating the discharge plasma under the pressure near the atmospheric pressure is proposed, for example, the method of processing under a helium ambient atmosphere to JP,2-48626,A is indicated, and becomes JP,4-74525,A from an argon, an acetone, and/or helium is indicated.
[0006] However, each above-mentioned approach is an approach of generating the plasma in the gas ambient atmosphere containing helium or an acetone, a gas ambient atmosphere is limited and sufficient electron density for a diamond-like carbon thin film to generate is not obtained under these gas ambient atmospheres. For this reason, under the pressure near the atmospheric pressure, the attempt which is going to make a diamond-like carbon thin film was not made.
[0007]
[Problem(s) to be Solved by the Invention] This invention is made in order to solve the above problems, it generates homogeneity and the high discharge plasma of electron density under the pressure near the atmospheric pressure, and offers the approach of manufacturing a diamond-like carbon thin film at a

high speed and low temperature on a base material front face.
[0008]
[Means for Solving the Problem] the manufacture approach of the diamond-like carbon thin film invention (henceforth the 1st invention) of this application according to claim 1 be characterize by generating a discharge plasma by impressing the pulse-ized electric field between the counterelectrodes concerned under the gas ambient atmosphere which install a solid dielectric in one [at least] opposed face of a counterelectrode, and contain oxygen and/or hydrogen in a carbon list under the pressure near the atmospheric pressure.
[0009] the manufacture approach of the diamond-like carbon thin film invention (henceforth the 2nd invention) of this application according to claim 2 -- the 1st invention -- setting -- the discharge current consistency between counterelectrodes -- 0.2 - 300 mA/cm2 it is -- it is characterized by using the discharge plasma.
[0010] The manufacture approach of the diamond-like carbon thin film invention (henceforth the 3rd invention) of this application according to claim 3 is characterized by impressing the pulse electric field build up time and/or whose falling time amount are 40ns - 100 microseconds and whose field strength is 1 - 100 kV/cm in the 1st invention or the 2nd invention.
[0011] The manufacture approach of the diamond-like carbon thin film invention (henceforth the 4th invention) of this application according to claim 4 is characterized by making the frequency in the pulse-ized electric field with 1-100kHz, and making pulse length with 1 - 1000 microseconds in the 1st invention, the 2nd invention, or the 3rd invention.
[0012] In the above-mentioned invention, since the 1st invention - the 4th invention are invention relevant to mutual, they explain these to this invention, a call, and the following collectively [the invention].
[0013] In this invention, the bottom of the pressure near the atmospheric pressure points out the bottom of the pressure of 100 - 800Torr. Pressure regulation is easy and the range of 700 - 780Torr where equipment becomes simple is desirable.
[0014] The plasma generating approach of this invention has the counterelectrode of a pair, and is performed in the equipment with which the solid dielectric is installed at least in one side of the opposed face of the electrode concerned. When a solid dielectric is installed in one side of the above-mentioned electrode, the part which the plasma generates is the space between solid dielectrics between a solid dielectric and an electrode, when a solid dielectric is installed in the both sides of the above-mentioned electrode.
[0015] As the above-mentioned electrode, what consists of alloys, such as metal simple substances, such as copper and aluminum, stainless steel, and brass, an intermetallic compound, etc. is mentioned. In order to avoid generating of the arc discharge by electric-field concentration, as for the above-mentioned counterelectrode, it is desirable that it is the structure where the distance between counterelectrodes serves as abbreviation regularity. As electrode structure of fulfilling this condition, an parallel monotonous mold, a cylinder opposite monotonous mold, a ball opposite monotonous mold, a hyperboloid opposite monotonous mold, coaxial-circles telescopic structure, etc. are mentioned.
[0016] The above-mentioned solid dielectric is installed in one side or the both sides of an opposed face of the above-mentioned electrode. Under the present circumstances, a solid dielectric and the near electrode installed stick, and the opposed face of the touching electrode is covered completely. When there is a part where electrodes counter directly, without being covered with a solid dielectric, it is for arc discharge to arise from there.
[0017] As the above-mentioned solid dielectric, multiple oxides, such as metallic oxides, such as plastics, such as polytetrafluoroethylene and polyethylene terephthalate, glass, a silicon dioxide, an aluminum oxide, a zirconium dioxide, and a titanium dioxide, and barium titanate, etc. are mentioned.
[0018] Although the shape of the shape of a sheet and a film has as the configuration of the above-mentioned solid dielectric, it is desirable that thickness is 0.05-4mm. It is to take the high voltage to generate the discharge plasma, if too thick, for dielectric breakdown to happen at the time of electrical-potential-difference impression, if too thin, and for arc discharge to occur.

[0019] Although the above-mentioned inter-electrode distance is determined in consideration of the purpose using the thickness of a solid dielectric, the magnitude of applied voltage, and the plasma etc., it is desirable that it is 1-50mm. Less than 1mm is not enough to keep and install inter-electrode spacing. If it exceeds 50mm, it is difficult to generate the uniform discharge plasma.
[0020] The example of a pulse voltage waveform is shown in drawing 1 . Wave (A) and (B) are [a square wave mold and wave (D) of an impulse mold and wave (C)] the waves of a modulation mold. Although electrical-potential-difference impression mentioned what is the repeat of positive/negative to drawing 1 , the pulse of the type which impresses an electrical potential difference to a forward or negative polarities [one of] side may be used.
[0021] Although the pulse voltage waveform in this invention is not limited to the wave mentioned here, ionization of the gas in the case of plasma generating is efficiently performed, so that the build up time and falling time amount of a pulse are short.
[0022] It is desirable especially that the build up time and/or falling time amount of a pulse are 40ns - 100 microseconds, and it is 50ns - 5 microseconds more preferably. In less than 40ns, if it is not realistic and exceeds 100 microseconds, a discharge condition will become unstable that it is easy to shift to an arc. In addition, as for the time amount whose electrical-potential-difference change is forward continuously, and falling time amount, as for build up time here, electrical-potential-difference change shall point out the time amount which is negative continuously.
[0023] Furthermore, you may become irregular using pulse shape, build up time, and the pulse from which a frequency differs. It is suitable for such a modulation performing high-speed continuation manufacture.
[0024] As for the frequency of pulse electric field, it is desirable that it is 1kHz - 100kHz. Processing takes time amount too much as it is less than 1kHz, and if it exceeds 100kHz, it will become easy to generate arc discharge.
[0025] Moreover, as for pulse length, it is desirable that it is 1 microsecond - 1000 microseconds, and it is 3 microseconds - 200 microseconds more preferably. Discharge becomes being less than 1 microsecond with an unstable thing, and if it exceeds 1000 microseconds, it will become easy to shift to arc discharge. In here, although the above-mentioned pulse length has shown the example in drawing 2 , it means the time amount in the pulse electric field which consist of a repeat of ON and OFF which a pulse follows. By the pulse of an intermittent mold like drawing 2 (a), although pulse length is equal to pulse width time amount, unlike pulse width time amount, in a wave-like pulse like drawing 2 (b), time amount including two or more of a series of pulses is said.
[0026] Furthermore, in order to stabilize discharge, it is desirable to have the OFF time amount continued for at least 1 microsecond in 1ms of charging time values.
[0027] The above-mentioned discharge is performed by impression of electric field. Although the magnitude of electric field is decided suitably, in this invention, it is desirable to make it the range in which inter-electrode field strength serves as 1 - 100 kV/cm. Diamond thin film formation takes time amount too much as field strength is less than 1 kV/cm, and if cm is exceeded in 100kV /, it will become easy to generate arc discharge. Moreover, a direct current may be superimposed in impression of the above-mentioned pulse voltage.
[0028] The block diagram of the power source at the time of impressing such pulse electric field to drawing 3 is shown. Furthermore, the representative circuit schematic of a power source is shown in drawing 4 . What is being described as SW at drawing 4 is a semiconductor device which functions as a switch. By using the semiconductor device which has the turn-on time and the turn-off time for 500 or less ns as the above-mentioned switch, a high voltage [as / whose above field strength is 1 - 100 kV/cm / whose build up time and falling time amount of a pulse are 40ns - 100 microseconds], and high-speed pulse electric field are realizable.
[0029] Hereafter, with reference to the representative circuit schematic of drawing 4 , the principle of a power source is explained briefly. + E is the direct-current-voltage feed zone of straight polarity, and -E is the direct-current-voltage feed zone of negative polarity. SW 1-4 is a switching device which consists of above high-speed semiconductor devices. D 1-4 shows diode. I1 - I4 The flow direction of a current is

expressed.
[0030] When SW1 turns ON in the first place, the load of straight polarity is a current I1. A flow direction is charged. Next, by turning ON SW2 in an instant, after SW1 is turned off, the charged charge passes along SW2 and D4, and it is I3. It charges in a direction. After SW2 is turned off, when SW3 is turned ON next again, the load of negative polarity is a current I2. A flow direction is charged. Next, by turning ON SW4 in an instant, after SW3 is turned off, the charged charge passes along SW4 and D2, and it is I4. It charges in a direction. Actuation of a top Norikazu ream can be repeated and the output pulse of drawing 5 can be obtained. This table of operation is shown in Table 1.
[0031]
[Table 1]

	①	②	③	④	⑤
SW1	OFF	ON	OFF	OFF	OFF
SW2	OFF	OFF	ON	OFF	OFF
SW3	OFF	OFF	OFF	ON	OFF
SW4	OFF	OFF	OFF	OFF	ON

[0032] The point which can discharge the charge charged certainly by operating SW2, D4, or SW4 and D2 even if the advantage of this circuit is the case that the impedance of a load is high, And it is in the point that it can charge at a high speed using SW1 and SW3 which are the switching device of a high-speed turn-on, and, for this reason, the very early pulse signal of build up time and falling time amount can be obtained like drawing 5 .
[0033] the discharge obtained by the above-mentioned approach -- setting -- the discharge current consistency between counterelectrodes -- 0.2 - 300 mA/cm2 it is -- things are desirable.
[0034] When the above-mentioned discharge current consistency means the value which **(ed) the current value which flows to inter-electrode by discharge in the area of the direction which intersects perpendicularly with the flow direction of the current in discharge space and the thing of an parallel monotonous mold is used as an electrode, it is equivalent to the value which **(ed) the above-mentioned current value by the opposed face product. Although a pulse-like current flows in this invention in order to form pulse electric field in inter-electrode, the value which **(ed) the maximum of that pulse current, i.e., peak to peak value, in the above-mentioned area is said in this case.
[0035] 0.2-300mA/cm2 which it is shown clearly by research of this invention persons in the glow discharge under the pressure near the atmospheric pressure that it is the value to which a discharge current consistency influences manufacture of a diamond-like carbon thin film reflecting a plasma consistency, and described above the inter-electrode discharge current consistency By considering as the range, the discharge plasma which is homogeneity and high electron density is generated, and the manufacture result of a good diamond-like carbon thin film can be obtained.
[0036] In this invention, the discharge plasma is generated under the gas (it is hereafter called material gas) ambient atmosphere which contains oxygen and/or hydrogen in a carbon list. Although each may exist as another compound, a compound may be used for the above-mentioned material gas for the compound which has carbon and oxygen, the compound which has carbon and hydrogen, carbon, oxygen, and hydrogen, for example.
[0037] When material gas is illustrated concretely, alcoholic system gas, such as a methanol and ethanol Alkane system gas, such as methane, ethane, a propane, butane, a pentane, and a hexane Alkene system gas, such as ethylene, a propylene, a butene, and a pentene, pentadiene, Alkyne system gas, such as alkadiene system gas, such as a butadiene, acetylene, and methylacetylene Aromatic hydrocarbon system gas, such as benzene, toluene, a xylene, an indene, naphthalene, and a phenanthrene Oxygenated carbon compound system gas, such as cycloalkene system gas, such as cycloalkane system gas, such as a cyclopropane and a cyclohexane, cyclopentene, and a cyclohexene, a carbon monoxide, and a carbon dioxide, etc. is mentioned, and these at least one sort can be used.
[0038] When using two or more sorts of above-mentioned carbon content gas, it is desirable to use the

choke damp as one constituent, and, as for the rate, it is desirable as a mixed ratio of the carbon content gas / choke damp other than the choke damp that it is 1 / 1 - 1/3 (vol ratio). The ratio of the choke damp is advantageous on the improvement in a formation rate of a diamond-like carbon thin film in it being the above-mentioned range.

[0039] 2 - 80vol% of the concentration occupied in the gas ambient atmosphere of carbon content gas is desirable. If the formation rate of a diamond-like carbon thin film falls and 80vol% is exceeded when concentration is less than [2vol%], the thin film obtained will become graphite-like.

[0040] Oxygen and hydrogen are under discharge, and become atom-like, and it has the effectiveness of removing alternatively the graphite generated to a diamond and coincidence. In order to make oxygen and hydrogen exist in a gas ambient atmosphere, oxygen gas (O2) and hydrogen gas (H2) may be used besides using the gas of the above mentioned organic compound. When using oxygen gas or hydrogen gas, as for the concentration occupied in the gas ambient atmosphere of oxygen gas or hydrogen gas, it is desirable not to exceed 70vol%. When exceeding 70vol(s)%, the thin film obtained becomes graphite-like conversely.

[0041] Moreover, the above-mentioned material gas may be diluted with gas other than the gas which contains oxygen and/or hydrogen in a carbon list. Especially the thing for which dilution gas is used is desirable from a viewpoint of safety. As dilution gas used by this invention, the gas and the nitrogen gas of an element of the 0th group of periodic law are mentioned, and these at least one sort can be used. If it illustrates concretely, helium, an argon, neon, a xenon, nitrogen gas, etc. will be mentioned. 20 - 90vol% of the concentration occupied in the gas ambient atmosphere of dilution gas is desirable. If the thin film with which the above-mentioned concentration is obtained in the case of below 20vol% becomes graphite-like and exceeds 90vol%, the formation rate of a diamond-like carbon thin film will fall.

[0042] Furthermore, the property as a semi-conductor can also be raised by adding the gas containing boron elements, such as diboron hexahydride (BH3 BH3) and phosphines (PH3, CH3 PH2, etc.), and a phosphorus element to the gas ambient atmosphere at the time of discharge, and forming a thin film.

[0043] Hereafter, the approach of manufacturing a diamond-like carbon thin film on a base material front face is explained in full detail. The approach of this invention has the counterelectrode of a pair, when a solid dielectric is installed in one side of the above-mentioned electrode and it installs a solid dielectric in the space between a solid dielectric and an electrode, and the both sides of the above-mentioned electrode in the equipment with which the solid dielectric is installed at least in one side of the opposed face of the electrode concerned, it installs a base material in the space of solid dielectrics, and it processes a base material front face by the discharge plasma generated all over the space concerned.

[0044] As a base material used for this invention, plastics, such as polyethylene, polypropylene, polystyrene, a polycarbonate, polyethylene terephthalate, a polyphenylene ape fight, a polyether ether ketone, polytetrafluoroethylene, and acrylic resin, glass, a ceramic, a metal, etc. are mentioned. Especially as a configuration of a base material, it is not limited and can apply to the base material which has the shape of tabular and a film, and various solid configurations.

[0045] An example of equipment which performs the manufacture approach of this invention to drawing 6 is shown. In this equipment, the solid dielectric 16 is installed on the lower electrode 15, and the discharge plasma occurs to the space between a solid dielectric 16 and the up electrode 14. The container 12 is equipped with the gas installation tubing 18, gas exhaust 20, and the flueing opening 21, and material gas is supplied to the discharge plasma generating space 13 from the gas installation tubing 18. In this invention, since a diamond-like carbon thin film is formed in the part in contact with the generated discharge plasma, this thin film is formed in the top face of a base material 17 in the example of drawing 6 . What is necessary is to float on the discharge plasma generating space 13 and just to install a base material in it to give this thin film to both sides of a base material.

[0046] As for a controlled atmosphere, it is desirable that plasma generating space is supplied at homogeneity. When performing discharge plasma treatment in the controlled atmosphere which consists of the mixture of gas of material gas and dilution gas, since the specific gravity difference is large, it is desirable that are easy to become an ununiformity at the time of supply, and a device of equipment

which avoids this is made. In the example shown in the equipment of drawing 6 , the gas installation tubing 18 is connected with the up electrode 14 with porous structure, and material gas is supplied to the plasma generating space 13 from the base material upper part through the hole of the up electrode 14, after being mixed by the gas blender which is not illustrated. Dilution gas is supplied through the dilution gas installation tubing 19 apart from this. A gas will not be limited to such structure, if supply to homogeneity is possible, but means, such as spraying a gas at stirring or a high speed, may be used.
[0047] The quality of the material of the above-mentioned container 12 is not especially limited, although resin, glass, etc. are mentioned. If it has structure which was able to take the electrode and the insulation, metals, such as stainless steel and aluminum, can also be used.
[0048]
[Embodiment of the Invention] Hereafter, in order to explain the approach of this invention in more detail, it has an example and explains below. The power source (made in Heiden, the product made from semiconductor device:IXYS, and part number TO-247AD are used) by the representative circuit schematic of drawing 4 was used for the power source. Moreover, the evaluation approach of the obtained diamond-like carbon thin film is as follows.
[0049] identification Raman of the evaluation approach (1) film -- a spectrum -- it identified that the obtained thin film was a diamond-like carbon thin film by using equipment (the product made from Nicolet, Raman 950), performing Raman spectroscopic analysis of the obtained thin film, and checking the existence of the peak value (1332-/cm) of the Raman spectrum which belongs to a diamond.
(2) membranous description -- it evaluated by observing the diameter of crystal grain of profit ****** with a scanning electron microscope (the Hitachi, Ltd. make, EP-2000).
[0050] The discharge plasma treatment equipment shown in example 1 drawing 6 was used, and the content volume of the chamber is made of the container 12 made from stainless steel in 10l. The diameter was 140mm, and the lower electrode 15 covered the front face with the zirconium dioxide dielectric 16 of specific inductive capacity 16, and has arranged the silicon substrate 17 on it. The up electrode 14 has been arranged from the base material front face to 2mm upper part. The diameter was 80mm, the hole with a diameter of 1mm arranged the up electrode 14 at intervals of 5mm on it, and it covered the front face with the zirconium dioxide dielectric of specific inductive capacity 16.
[0051] Using the oil sealed rotary pump, it exhausted until the inside of the above-mentioned discharge plasma treatment equipment was set to 0.1Torr(s), and nitrogen gas was introduced until the inside of equipment was set to 760Torr(s) from the dilution gas installation tubing 19. Introducing the mixture of gas of acetylene 2sccm and nitrogen gas 998sccm into after an appropriate time from the gas installation tubing 18 linked to an up electrode, the peak value of 18kV, the frequency of 8kHz, 500ns of rates of rise, and pulse electric field of 20 microseconds of pulse length were impressed between the up electrode 14 and the lower electrode 15, discharge was performed for 3 minutes, and the diamond-like carbon thin film was formed. In addition, a discharge current consistency is 2 60mA/cm. The substrate temperature under membrane formation was 100 degrees C.
[0052] As a result of the approach which described the obtained thin film above estimating, the peak which belongs to the diamond of 1333-/cm was checked by Raman spectroscopic analysis, and the crystallized state of the diamond with which a particle with a particle size of 0.3-1 micrometer is located in a line with the whole surface was observed in scanning electron microscope observation. It was 0.5 micrometers in the place and five-point average which measured thickness from cross-section observation. So, the membrane formation rate at this time is 1. They were mum / time amount.
[0053] As example 2 carbon content gas, the diamond-like carbon thin film was formed like the example 1 except having used ethyl alcohol 25sccm. As a result of evaluating the obtained thin film, the peak which belongs to the diamond of 1333-/cm was checked by Raman spectroscopic analysis, and the diamond crystallized state to which a particle with a particle size of 0.3-1 micrometer is located in a line with the whole surface was observed in scanning electron microscope observation. The membrane formation rate was 0.8micrometers/hour.
[0054] The diamond-like carbon thin film was formed like the example 1 except having used example 3 substrate as the soda glass substrate. As a result of evaluating the obtained thin film, the peak which

belongs to the diamond of 1333-/cm was checked by Raman spectroscopic analysis, and the crystallized state to which a particle with a particle size of 0.3-1 micrometer is located in a line with the whole surface was observed in scanning electron microscope observation. The membrane formation rate was 1micrometer/hour.

[0055] To the same gas combination as example of comparison 1 example 1, and a substrate, the sine wave of 15kHz and 150W was added, and membrane formation of a diamond-like carbon thin film was tried. Although discharge was produced, change was not seen on the substrate, the peak which belongs to a diamond by Raman spectroscopic analysis was not acquired, and, as for the deposit of a particle special to a substrate front face, after discharge of 1 hour was not seen in scanning electron microscope observation.

[0056]

[Effect of the Invention] Since the manufacture approach of this invention is constituted as mentioned above, a diamond-like carbon thin film is near the atmospheric pressure, and can form it on a substrate at a high speed at low temperature. Therefore, since it can apply also to a heat-resistant low base material and surface treatment can be economically done near the atmospheric pressure rather than before at high speed, the application application range is used suitable for breadth, for example, transparence lighting material, transparence electric conduction material, the surface protective layer of a cutting tool, the charge of optical material, an electronic ingredient, a chemical-industry ingredient, etc.

[0057]

[Translation done.]